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RECENT INVESTIGATIONS ON THE CURRENT STATUS OF UNDERSTANDING ON THE ANODIC BEHAVIOUR OF NICKEL IN FLUORIDE MEDIA

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In fluoride media, a passive layer of nickel fluoride is easily formed on nickel surfaces during anodic polarisation. This film remains insoluble in liquid HF, non-aqueous fluoride media, low temperature melts and even in HF media containing upto 20% water. In aprotic media, the fluoride film formed is generally uniform. Nucleative processes become quite significant when the acidity is low. Acidity appears to play a significant role in dissolving the oxide layer and enhancing uniform dissolution and precipitation of nickel fluoride. Around 3.0 V, the anodic fluoride film exhibits finite resistivity and allows charge transfer. The resistivity of the film itself exhibits some potential dependence. The electron transfer probably leads to the formation of high valent NiF_2 such as NiF_3 or nickel fluoride embedded with free radical fluorine. The voltammetric responses in liquid HF, aprotic fluoride media as well as low temperature fluoride melts are being investigated at present.

Keywords: Passivation, anodic behaviour, nickel electrode

INTRODUCTION

Nickel is generally one of the very stable metals in fluoride media. Nickel and nickel-alloys generally are the materials of choice for handling fluorine and HF especially at high temperatures. In liquid HF, nickel is the only anode material of choice for electrochemical perfluorination processes. Even in molten electrolyte media, nickel anodes are used wherever very high purity of fluorinating gases like NF_3 free from CF_4 are required. Despite such a wide range of electrochemical applications for nickel, there are very few investigations on the anodic behaviour of nickel in different fluoride media.

In recent times this laboratory has undertaken a series of investigations on the anodic behaviour of nickel in aqueous and non-aqueous fluoride media. In what follows, a comprehensive overview of recent findings in this area specifically originating from this laboratory is presented. Cyclic voltammetry was the predominant technique employed. In addition, however, other experimental techiques have also been employed. These are described in detail in the respective references cited.

RESULTS AND DISCUSSION

Anodic behaviour of nickel in aqueous media

In dilute aqueous HF solutions, nickel undergoes facile dissolution. However, a thin salt layer of NiF_2 film is quite easily formed on the surface of nickel electrode. The voltammetric responses in 2 *M* aqueous HF solutions, at different sweep rates presented in Fig. 1 correspond to this film dissolution precipitation model. The experimental response (points) also corresponds well with theoretically expected voltammograms (continuous line). In the voltammetric time scale, the NiF_2 film gets dissolved completely within a few minutes under open circuit condition [1,2].

In HF solution of higher concentration, two distinct dissolution precipitation processes are observed during the forward as well as reverse sweep. Typical experimental

cyclic voltammograms along with theoretical responses are presented in Fig. 2. The theoretical model assumes two distinct anodic dissolution processes with two different film resistivity. In aqueous media of low HF concentration, the anodic dissolution always proceeds through the oxide layer present on the nickel surface. With increasing HF content, part of the oxide layer is chemically dissolved by the acidic fluoride media. This results in two dissolution possibilities namely direct dissolution of oxide free nickel surface and through film dissolution of nickel surface covered with the oxide layer. These films also exhibit time dependent dissolution behaviour. The effect of sweep rate presented in Fig. 3 exhibits this time dependent dissolution behaviour [1,2].

Effect of monovalent cations

In general, the influence of pH and the attack of anodic species on the anodic dissolution of metals are well known. However, the likely influence of cationic species on the dissolution behaviour is not sufficiently recognised in corrosion science. Some investigations carried out in 1 *M* $HClO_4$ acid media clearly indicate the influence of monovalent cationic species on the anodic dissolution of Ni in fluoride media (Fig. 4). Typical cyclic voltammograms of 100 mM HF and 20 mM KF in 1 *M* $HClO_4$ under otherwise identical experimental conditions are presented in Fig. 4. Despite lower fluoride ions concentration, the anodic dissolution in KF is significantly higher and the dissolution processes also occur over a wider potential range. The dissolution of nickel especially in the more anodic potential region (beyond 0.8 V) is presumably due to the cation assisted dissolution of NiF_2 film as $KNiF_3$ and K_2NiF_4 which are highly soluble in aqueous medium [3].

The effect of monovalent cations may also be clearly seen in cyclic voltammetric responses of nickel in 1.0 *M* $HClO_4$, media containing 0.1 *M* concentration of NH_4F, NaF and LiF as shown in Fig. 5. Hydrated Li ions also assist the anodic

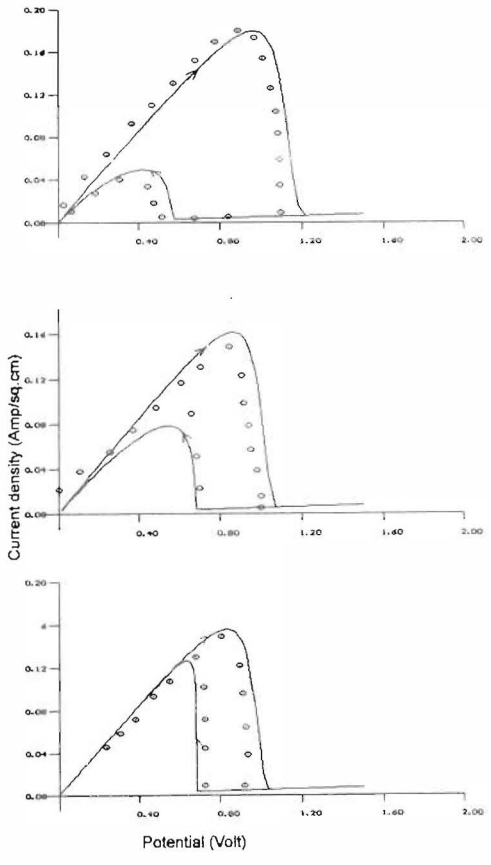

Fig. 1: Experimental (000) and theoretical (---) CV of Ni in 2 M HF. Influence of sweep rate (mVs^{-1}) (a) v = 10, (b) v = 80 and (c) v = 160

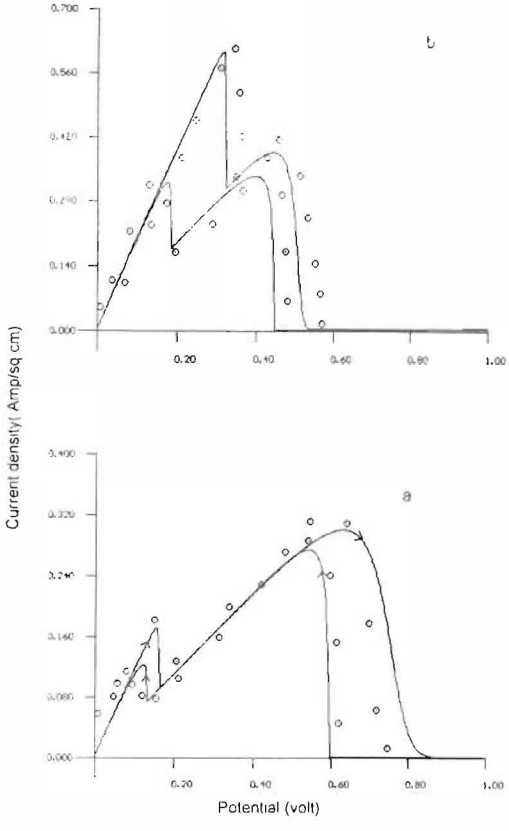

Fig. 2: Experimental (000) and theoretical (---) CV of Ni in HF of concentration (a) 10 M and (b) 20 M at same v = 10 (mVs^{-1})

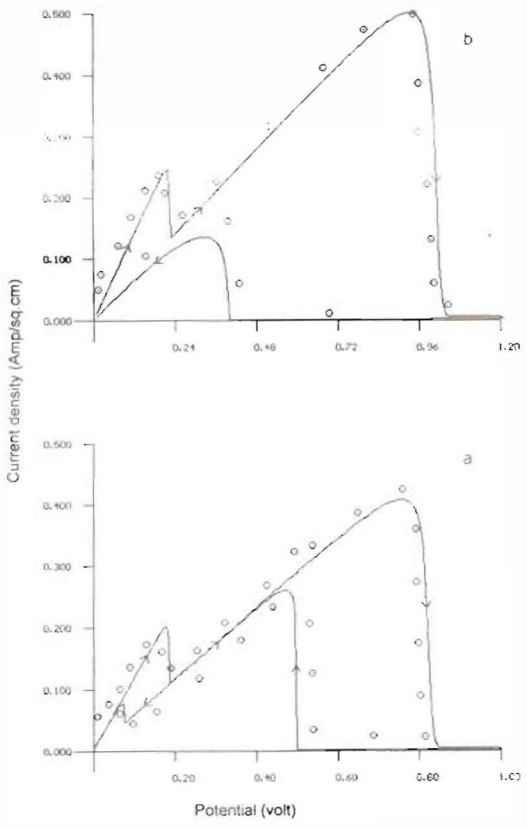

Fig. 3: Experimental (000) and theoretical (---) CV of Ni in 10 M at (a) v = 50 (mVs^{-1}) and (b) v = 200 (mVs^{-1})

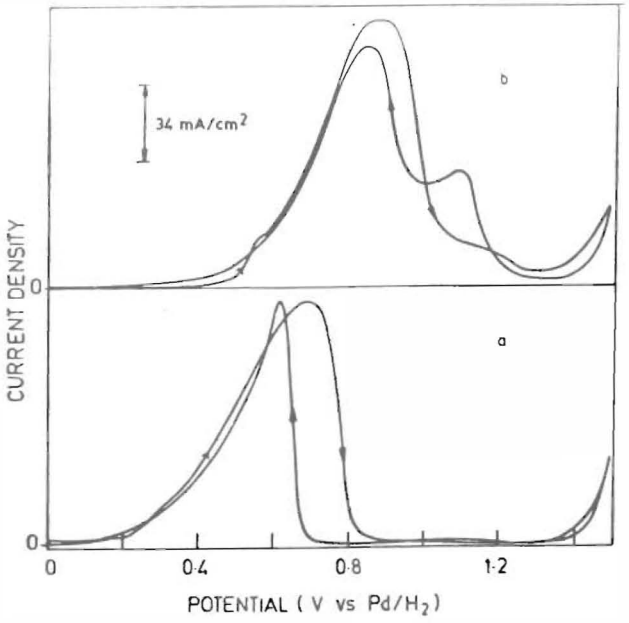

Fig. 4: CV of Ni in 1 M $HClO_4$ containing (a) 100 mM HF and (b) 20 mM KF at same v = 10 (mVs^{-1})

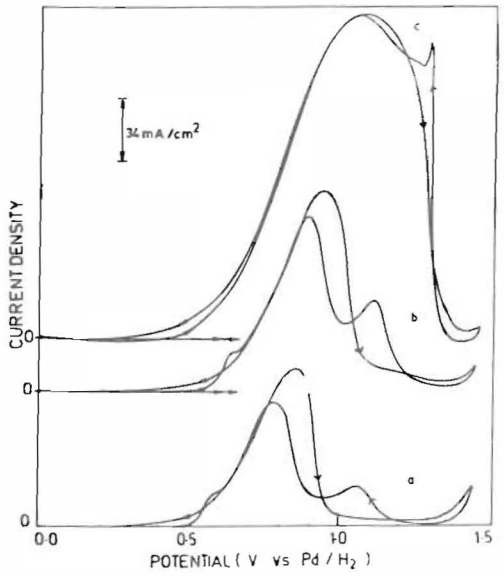

Fig. 5: CV of Ni in 1 M $HClO_4$ containing 100 mM of (a) NH_4F (b) NaF and (c) LiF at same v = 10 (mVs^{-1})

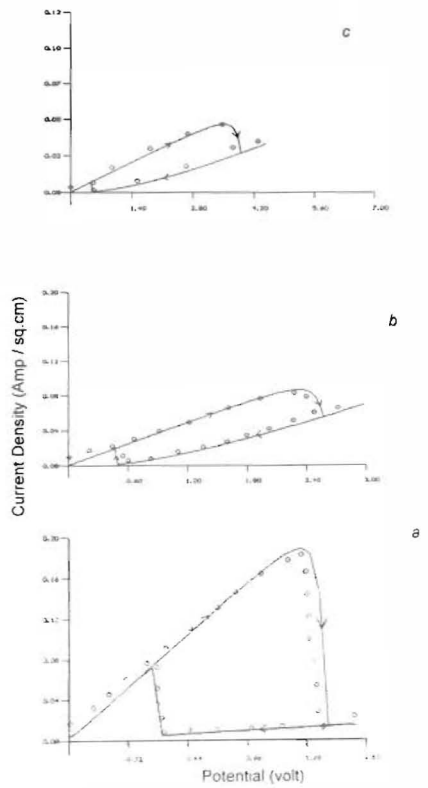

Fig. 6: Experimental (000) and theoretical (---) CV of Ni in CH_3CN–H_2O in 2 M HF. Influence of concentration of CH_3CN (a) 20%, (b) 40% and (c) 80% at same v = 10 (mVs^{-1})

dissolution process by enhancing the local acidity near the nickel surface. Hence, the anodic dissolution in LiF is considerably higher and also occurs on a much wider potential range [3].

Effect of solvents

The passive NiF_2 layer is highly soluble in aqueous media. In other solvents and solvent mixtures, the anodic dissolution behaviour is significantly different. Typical cyclic voltammograms of anodic dissolution of nickel in 2 *M* HF containing different ratios of CH_3CN and water under otherwise identical conditions are presented in Fig. 6. With increasing concentration of CH_3CN, the passivation potential corresponding to complete NiF_2 film formation shifts to more anodic regions. The dissolution of NiF_2 during the reverse sweep also decreases significantly. The resistivity of NiF_2 layer as shown by the slope of the current-potential curve in the reverse sweep also varies significantly with CH_3CN content in the solvent media [2,4].

The nature of the solvent also influences the voltammetric responses. Typical cyclic voltammograms of 2 *M* HF in aqueous mixtures containing 80% methanol, DMF and dioxane under otherwise identical experimental conditions are presented in Fig. 7. In aqueous methanolic mixtures, the NiF_2 layer is quite insoluble, but the passivation process is completed below 1.6 V. Considerably higher passivation potentials and lower film resistivity are noticed in DMF and dioxane mixtures [2,5].

Anodic behaviour in anhydrous HF/CH_3CN

In the absence of H_2O, NiF_2 film becomes highly stable and hence practically no dissolution of Ni is observed during the second and subsequent sweeps. The voltammetric responses however, still depend on the concentration of HF. Typical cyclic voltammograms obtained during anodic polarisation of Ni in 2 *M*, 4 *M* and 6 *M* AHF in CH_3CN media are shown in Fig. 8. In the second and subsequent sweeps the current potential curve practically retraces, the curve, during the first

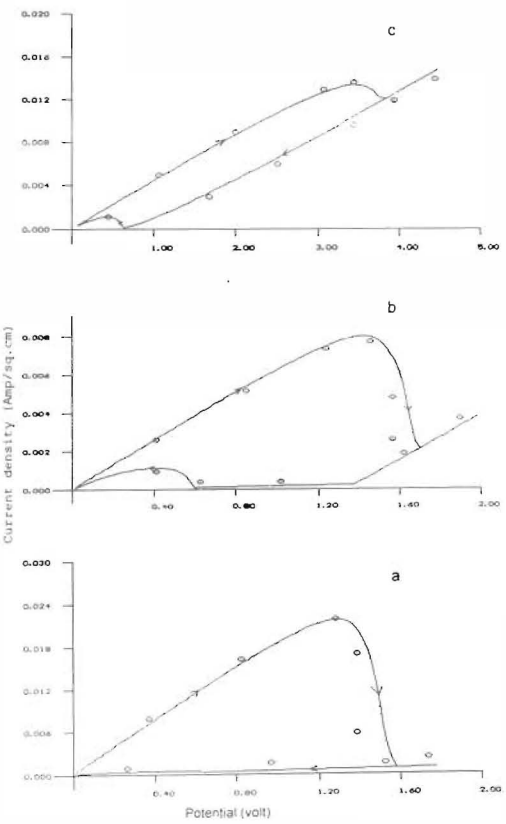

Fig. 7: Experimental (000) and theoretical (---) CV of Ni containing 2 M HF in (a) 80% methanol (b) 80% DMF and (c) 80% dioxane at same v = 10 (mVs^{-1})

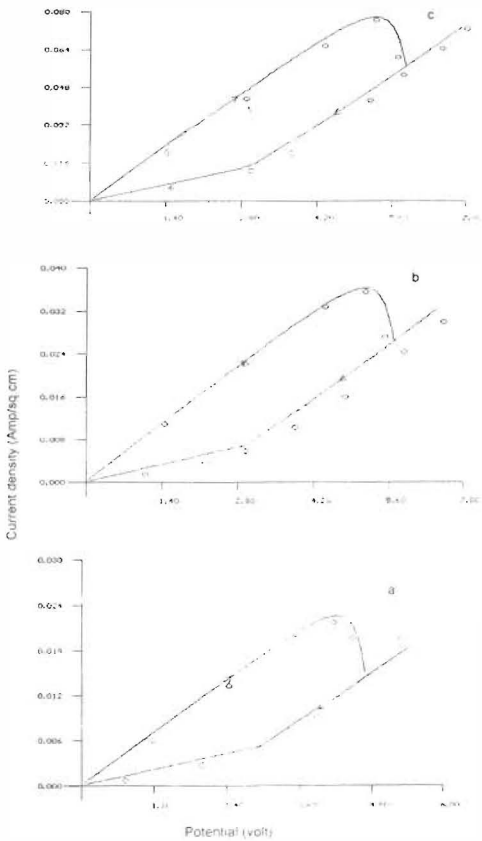

Fig. 8: Experimental (000) and theoretical (---) CV of Ni in CH_3CN containing AHF of concentration (a) 2, (b) 4 and (c) 6, v = 120 (mVs^{-1})

reverse sweep. The conductivity of the NiF_2 film also depends on HF concentration [2,6].

Addition of small quantity of water influences the voltammetry response quite significantly. This effect is shown in Fig. 9. The presence of small quantity of water improves the conductivity of NiF_2 film and also brings down the critical potential for the conductivity [2,6].

Effect of acidity in CH_3CN media

The acidity of HF dissolved in CH_3CN may be conveniently varied by the addition of Et_3N. This was also found to have significant effect on the anodic behaviour of Ni. Typical cyclic voltammograms obtained in 0.5 *M* (Et_3N . 6HF/CH_3CN) at different sweep rates are shown in Fig. 10. Around 0 V, an anodic dissolution peak corresponding to the formation of monolayer NiF_2 film is noticed. Further oxidation was noticed below 3 V. Scanning electron microscopic studies (SEM) and i-t transients measurements indicated that NiF_2 film growth occurs uniformly on the electrode surfaces, when the solution is sufficiently acidic as in this case [7]. When the Et_3N concentration is enhanced as in the case of 4.5 *M* (Et_3N 0.66 HF) the anodic behaviour changes substantially. The voltammetric responses obtained under this condition at different sweep rates are shown in Fig. 11. The NiF_2 film growth over the monolayer surface occurs through a nucleative film growth processes beyond 4.5 V. Other experimental evidences also supported the view, namely film growth mechanism itself depends on the acidity of the fluoride media [7].

CONCLUSION

The anodic dissolution, formation of a passive NiF_2 layer, conductivity of this passive layer, the stability and solubility of NiF_2 film and further growth and other electron transfer processes are found to depend significantly on the type of electrolyte, solvent, the concentration of fluoride ion and other ionic species present in the media. Hence, it is quite important to consider all these factors while interpreting the

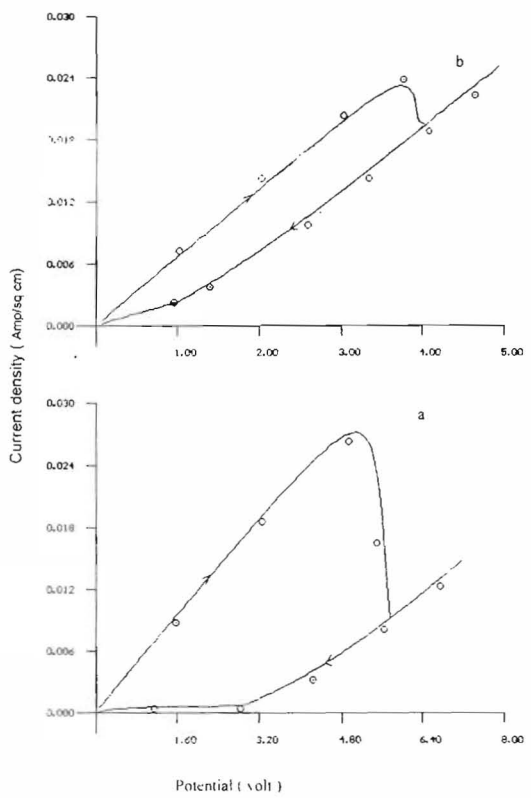

Fig. 9: Experimental (000) and theoretical (---) CV of Ni containing 2 M AHF/CH_3CN in (a) absence and (b) presence of 2 M H_2O at v = 120 (mVs^{-1})

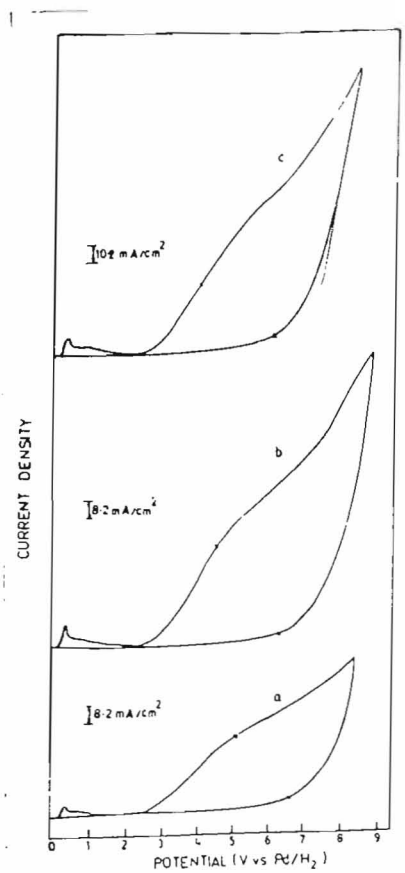

Fig. 10: CV of Ni in 0.5 M Et_3N . 6 HF/CH_3CN at different v (mVs^{-1}) (a) 60, (b) 120 and (c) 240

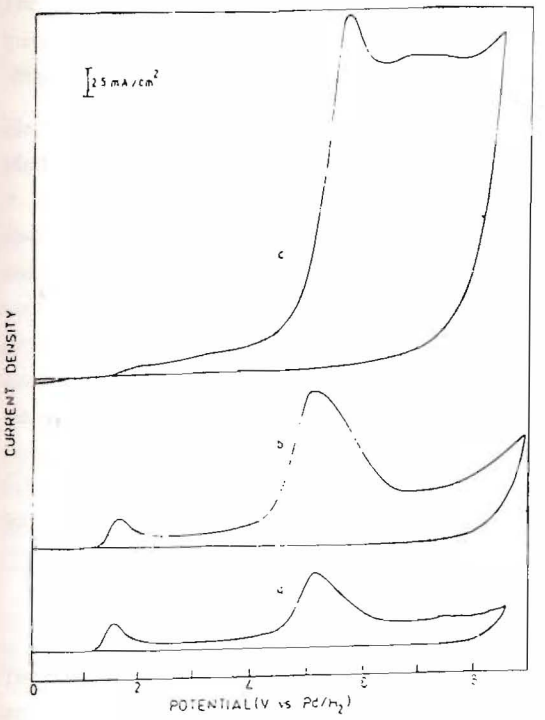

Fig. 11: CV of Ni in 4.5 M Et_3N . 0.66 HF/CH_3CN at different v (mVs^{-1}) (a) 60, (b) 120 and (c) 240

operating parameters on the anodic behaviour of Ni in different fluroride media.

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